



AFRL-RX-TY-TP-2011-0113

MODIFICATION OF POLY(VINYL BUTYRAL) COATINGS USING BIS-SILANES

Tammy L. Metroke
Universal Technology Corporation
1270 North Fairfield Road
Dayton, OH 45432

Michael V. Henley
Airbase Technologies Division
Air Force Research Laboratory
139 Barnes Drive, Suite 2
Tyndall Air Force Base, FL 32403-5323

Contract No. FA8650-07-D-5800-0055

April 2010

DISTRIBUTION A: Approved for release to the public; distribution unlimited.

**AIR FORCE RESEARCH LABORATORY
MATERIALS AND MANUFACTURING DIRECTORATE**

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 30-APR-2010	2. REPORT TYPE Journal Article - POSTPRINT	3. DATES COVERED (From - To) 01-MAY-2009 -- 01-MAR-2010		
4. TITLE AND SUBTITLE Modification of Poly(vinyl butyral) Coatings Using bis-silanes (POSTPRINT)		5a. CONTRACT NUMBER FA8650-07-D-5800-0055		
		5b. GRANT NUMBER		
		5c. PROGRAM ELEMENT NUMBER 0602102F		
6. AUTHOR(S) *Metroke, Tammy L.; ^Henley, Michael V.		5d. PROJECT NUMBER 4915		
		5e. TASK NUMBER L0		
		5f. WORK UNIT NUMBER Q220L8A2		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) *Universal Technology Corporation 1270 North Fairfield Road Dayton, OH 45432		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) ^Air Force Research Laboratory Materials and Manufacturing Directorate Airbase Technologies Division 139 Barnes Drive, Suite 2 Tyndall Air Force Base, FL 32403-5323		10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/RXQL		
		11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-RX-TY-TP-2011-0113		
12. DISTRIBUTION/AVAILABILITY STATEMENT Distribution Statement A. Approved for public release; distribution unlimited.				
13. SUPPLEMENTARY NOTES Ref AFRL/RXQ Public Affairs Case # 10-081. Document contains color images. Published in Progress in Organic Coatings 69 (2010) 470–474.				
14. ABSTRACT A commercially available poly(vinyl butyral) (PVB) coating was modified using a combination of 1–10 wt.% bis(trimethoxysilyl)benzene and dibutyltin dilaurate as the hydrolysis catalyst. Results of attenuated total reflectance (ATR)-FTIR analysis indicated the modification resulted in a hybrid coating material containing silicate moieties covalently bonded to the PVB polymer chains. Gravimetric analysis indicated the bis-silane addition resulted in a reduction in the diffusion coefficient of the parent coating to 2-chloroethyl ethyl sulfide (2-CEES), dimethyl methylphosphonate (DMMP), diisopropyl methylphosphonate, and methyl salicylate; the most significant reduction was observed for 2-CEES and DMMP at temperatures ≥50 °C. Glass transition temperature, abrasion resistance, tensile strength, and coating hardness were increased upon incorporation of the bis-silane. Despite incorporation of an inorganic component, coating flexibility was retained at low temperature (−15 °C).				
15. SUBJECT TERMS bis-silane, diffusion, barrier coatings, Poly(vinyl butyral)				
16. SECURITY CLASSIFICATION OF: a. REPORT U b. ABSTRACT U c. THIS PAGE U		17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 5	19a. NAME OF RESPONSIBLE PERSON Michael Henley
				19b. TELEPHONE NUMBER (Include area code)

Reset

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39-18



Modification of poly(vinyl butyral) coatings using bis-silanes

Tammy L. Metroke ^{a,*}, Michael V. Henley ^b

^a Universal Technology Corporation, 139 Barnes Dr., Suite 2, Tyndall AFB, FL 32403, USA

^b Air Force Research Laboratory, Airbase Technologies Division, 139 Barnes Dr., Suite, Tyndall AFB, FL 32403, USA

ARTICLE INFO

Article history:

Received 19 May 2010

Accepted 19 August 2010

Keywords:

Bis-silane

Diffusion

Barrier coatings

Poly(vinyl butyral)

ABSTRACT

A commercially available poly(vinyl butyral) (PVB) coating was modified using a combination of 1–10 wt.% bis(trimethoxysilyl)benzene and dibutyltin dilaurate as the hydrolysis catalyst. Results of attenuated total reflectance (ATR)-FTIR analysis indicated the modification resulted in a hybrid coating material containing silicate moieties covalently bonded to the PVB polymer chains. Gravimetric analysis indicated the bis-silane addition resulted in a reduction in the diffusion coefficient of the parent coating to 2-chloroethyl ethyl sulfide (2-CEES), dimethyl methylphosphonate (DMMP), diisopropyl methylphosphonate, and methyl salicylate; the most significant reduction was observed for 2-CEES and DMMP at temperatures $\geq 50^\circ\text{C}$. Glass transition temperature, abrasion resistance, tensile strength, and coating hardness were increased upon incorporation of the bis-silane. Despite incorporation of an inorganic component, coating flexibility was retained at low temperature (-15°C).

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Recent studies have shown that organic-inorganic interpenetrating networks, copolymers, and hybrid materials may be prepared via incorporation of novel functionalities into organic polymer systems using polysiloxanes [1], silicones [2], and alkoxide [3–5] precursors. Incorporation of an inorganic component into an organic polymer has been shown to result in modification of material properties including density, adhesion, transparency, thermal stability, and permeability. For example, Patil et al. [6] found that membranes based on poly(vinyl alcohol) crosslinked with tetraethyl orthosilicate (TEOS) were useful as oxygen barriers. Annenkov et al. [7] investigated the reaction of poly(vinyl butyral) with TEOS. Prezzi and Masscia [8] found that incorporation of alkoxy silanes into epoxy coatings resulted in a dense epoxy-silica hybrid with an elevated glass transition temperature, T_g , and extensive suppression of molecular relaxation in the T_g region. Van Ooij and coworkers [9] incorporated bis-silanes into epoxy, acrylate, and urethane coatings and found a significant increase in corrosion resistance of metal substrates. Ji et al. [10] found that incorporation of glycidoxypropyltrimethoxysilane or aminopropyltrimethoxysilane [11] decreased water absorption of an epoxy coating. Similar research focused on the development and characterization of hybrid films formed from polyurethane-titania

[12], polyacrylate-titania [13], epoxy-silica-titania [14], and titania-epoxy systems [15].

The objective of this study was to synthesize and characterize a novel organic-inorganic composite material via modification of a commercially available poly(vinyl butyral) (PVB) coating with 1–10 wt.% bis(2-trimethoxysilyl)benzene (BB) and dibutyltin dilaurate (DBTDL) as a hydrolysis catalyst. The PVB polymer backbone comprises 1,2-dioxane rings, unreacted C-OH (alcohol) groups and a minor fraction of acetate functionalities. Depending on the synthesis conditions, a common polymer formulation may contain 76, 22, and 2% of the butyral, alcohol, and acetate functionalities, respectively [16]. Unlike alkoxy silanes that have been traditionally used for modification of organic systems, the silane used in this study was a bis-silane, whose general molecular formula may be represented by $(RO)_3Si-X-Si(OR)_3$, where R represents a hydrolyzable silicon alkoxide functionality and X represents a non-hydrolyzable connector group as shown in Fig. 1. Attenuated total reflectance (ATR)-FTIR spectroscopy was used to determine the incorporation mechanism of the silane in the PVB coating. Gravimetric analysis was used to determine the diffusion coefficient of various chemicals through the parent and modified coatings. Abrasion resistance, coating hardness, and tensile strength were determined using standard methods.

2. Experimental

2.1. Materials

ALARA 1116, a waterborne, strippable coating was chosen as the parent coating and was used as received (CarboLine, Co.).

* Corresponding author at: 139 Barnes, Suite 2, Tyndall AFB, FL 32403, USA.
Tel.: +1 850 283 6708.

E-mail address: tammy.metroke.ctr@tyndall.af.mil (T.L. Metroke).



Fig. 1. Molecular structure of bis(2-trimethoxysilyl)benzene (BB).

The manufacturer discloses that the coating comprises 35% PVB, 10% hydrated alumina, and 55% water. 2-Chloroethyl ethyl sulfide (2-CEES), dimethyl methylphosphonate (DMMP), diisopropyl methylphosphonate (DIMP), dibutyltin dilaurate (DBTDL), and methyl salicylate (MS) were obtained from Aldrich or Alfa Aesar and were used as received. Bis(2-trimethoxysilyl)benzene was obtained from Gelest and used as received.

2.2. Coating modification and deposition

In this study, 1–10 wt.% bis(2-trimethoxysilyl)benzene (BB) was incorporated into a commercially available PVB coating along with an aqueous (1 wt.%) DBTDL solution as the hydrolysis catalyst [17,18] and allowed to stir for 2 h prior to deposition. Coatings were prepared on a Teflon™ surface using a drawdown bar and were allowed to cure at ambient temperature for a minimum of one week prior to analysis. Dry coating thickness was measured using a digital micrometer and is reported as the average of seven measurements along the length of the coating. Dry coating thicknesses were found to be approximately 0.32–0.34 mm (12.8–13.6 mil).

2.3. Infrared analysis

Infrared analysis of the coatings was conducted using a Nicolet 6700 IR spectrometer using an ATR accessory. ATR-FTIR spectra were recorded using a resolution of 4 cm^{-1} and were an average of 32 scans.

2.4. Permeation study

Breakthrough times for the permeants were recorded at several temperatures ranging from 22 to 75°C using the general procedure described in ASTM E96. In our experimental method, 100 μL of simulant was placed in a crimp-top vial onto which a septum containing a 9.52 mm (3/8-in.) diameter hole and the coating sample was crimped. Fig. 2 diagrams the experimental setup. The vials were placed in an oven at the appropriate temperature, removed periodically, weighed, and returned to the oven. Depending on the temperature and permeant used, the experiment was conducted for a period of 1–3 days.

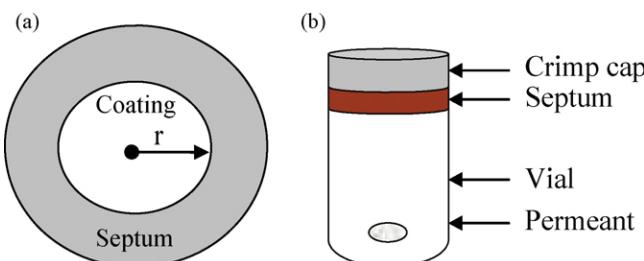


Fig. 2. (a) Representation of the exposure zone formed by the union of the coating with the septum and crimp top (top view); (b) complete vial assembly used for permeation studies. The coating was placed between the septum and the crimp cap.

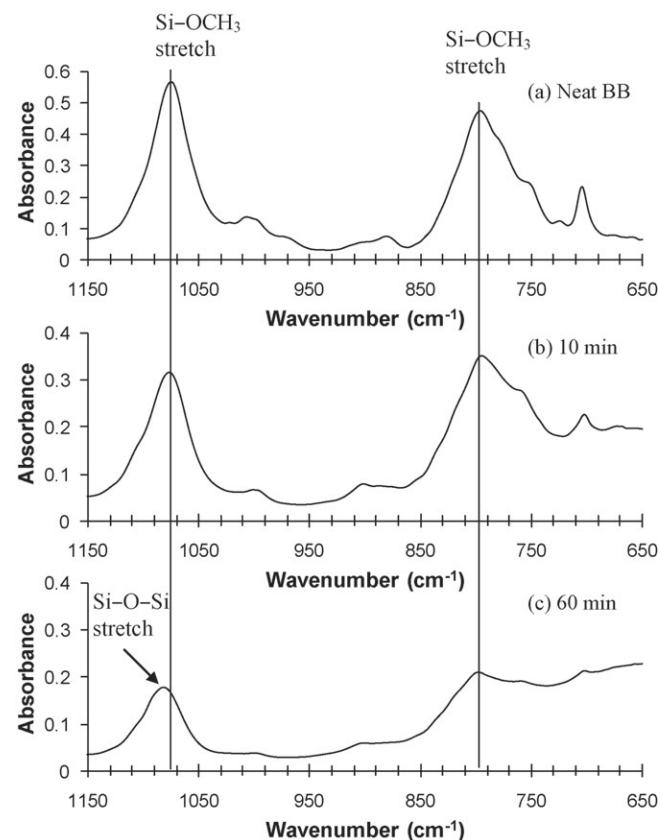


Fig. 3. ATR-FTIR analysis of the hydrolysis of BB using DBTDL as a hydrolysis catalyst of (a) the neat silane and after (b) 10 min and (c) 60 min hydrolysis.

2.5. Glass transition temperature

ATA Q1000 differential scanning calorimeter (DSC) was used to measure the T_g of the coating materials. DSC scans of the coatings were conducted in aluminum sample pans using a heating rate of $5^\circ\text{C}/\text{min}$ from -50 to 150°C .

2.6. Physical characteristics

Elongation and tensile strength of the coatings were determined in accordance with ASTM D 2370-98. Values reported are an average of five replicates. Coating hardness was determined using the pencil hardness test described in ASTM D 3363-05. Coating flexibility was determined using the low temperature mandrel bend test described in ASTM D 522 at 0 and -15°C . Coatings were allowed to acclimate at the test temperature for a minimum of 12 h and the test was conducted inside a freezer. Abrasion resistance was determined using a Taber abrader in accordance with ASTM D 4060 using four replicates per coating. Loss of coating thickness was determined after 1000 cycles.

3. Results and discussion

3.1. BB hydrolysis and condensation

Infrared spectroscopy has been used to study the hydrolysis and condensation reactions of silanes, including TEOS [19] and organically modified silanes [20–22] under various conditions. Prior to addition of the silane to the coating, ATR-FTIR was used to determine the fundamental hydrolysis and condensation mechanisms of BB in the presence of DBTDL. Fig. 3 shows infrared spectra of neat BB and the reaction with DBTDL as a function of time. BB exhibited two

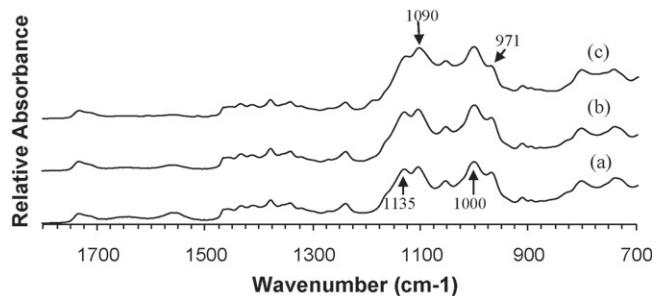


Fig. 4. ATR-FTIR spectra of the (a) parent coating and coatings modified using (b) 1 wt.% and (c) 10 wt.% BB. The arrows indicate (i) an increase in intensity of the band at 1090 cm^{-1} relative to that of the band at 1135 cm^{-1} due to the formation of Si—O—Si bonding in the coating and (ii) a decrease in intensity of the 971 cm^{-1} C—OH band relative to the 1000 cm^{-1} band due to Si—O—C bond formation.

strong bands due to Si—O—C stretching modes [23] of Si—OCH₃ at approximately 1075 and 798 cm^{-1} . As the hydrolysis reaction proceeded, the intensities of the 1075 and 798 cm^{-1} bands decreased. A new band was observed at approximately 1081 cm^{-1} , indicative of self-condensation resulting in the formation of siloxane (Si—O—Si) bonds [24]. From the perspective of our study, these results indicate that DBTDL-catalyzed hydrolysis of BB is initiated during the 2-h mixing period with the parent PVB solution prior to coating deposition; at this time, Si—OH groups are available for condensation with (a) C—OH groups on the PVB polymer to form Si—O—C bonds and (b) Si—OH groups from the hydrolyzed bis-silane to form Si—O—Si bonds.

3.2. Coating modification

Fig. 4 shows the ATR-FTIR spectra of the parent coating and the coatings modified using 1 and 10 wt.% BB. In the 900 – 1200 cm^{-1} region, the parent coating exhibited five characteristic bands centered at approximately 1135 , 1108 , 1058 , 1002 , and 971 cm^{-1} . The bands at 1135 , 1108 , and 1058 cm^{-1} were assigned to the C—O—C—O—C ring vibrations. The band at 971 cm^{-1} was assigned to the C—CO stretch in the alcohol functionality [23]. In the modified coatings, an increase in the intensity of the 1090 cm^{-1} band relative to that of the 1135 cm^{-1} band and a decrease in the intensity of the band at 971 cm^{-1} relative to that of the 1000 cm^{-1} band were observed.

The location of the new band in the ATR-FTIR spectra centered at approximately 1090 cm^{-1} indicates that siloxane (Si—O—Si) linkages were formed during the reaction. Additionally, the concomitant decrease in the intensity of the band centered at approximately 971 cm^{-1} due to the alcohol functionality, indicates condensation occurs between the partially hydrolyzed silane and C—OH groups on the polymer, crosslinking the inorganic and organic networks. Condensation likely occurred with acetal functionalities on the parent coating, though evidence for this was not observed in the ATR-FTIR analysis which we assumed was due to the low abundance of acetal functionalities in the parent coating. Based on these results, the modified coating comprises the bis-silane covalently bonded to the PVB coating and contains regions of Si—O—Si bonding dispersed throughout.

3.3. Coating characteristics

To understand the effect of BB addition on the properties of the parent PVB coating, the permeation characteristics, glass transition temperature (T_g), tensile strength, hardness, and flexibility were determined for the parent and modified coatings.

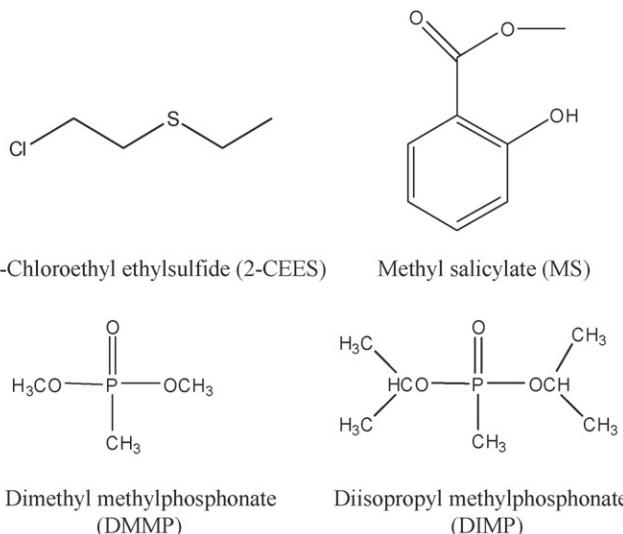


Fig. 5. Molecular structures of the permeants investigated.

3.3.1. Diffusion coefficient

Fig. 5 shows the molecular structures of the permeants investigated. Diffusion coefficient of a permeant molecule through a coating was estimated from mass loss vs. time plots as described in ASTM E96. Fig. 6 shows typical mass loss vs. time curves for the parent coating using DIMP as permeant at 60°C ; this curve is representative of data collected for the coatings, temperatures, and permeants investigated. To prepare this plot, the mass of the test assembly was measured periodically and was found to remain relatively constant (constant-mass region) indicating that the coating is exhibiting barrier properties toward the challenge simulant. After penetration, the mass of the vial decreased as the simulant permeates the coating; the slope of the mass loss is a measure of the steady-state permeation rate. The lag time, t_{lag} , was estimated as the intersection of linear fits through the constant-mass and the steady-state slope regions of the curve.

The diffusion coefficient, D , may be calculated from the coating thickness (l) and the lag time (t_{lag}) using Eq. (1) [25].

$$t_{lag} = \frac{l^2}{6D} \quad (1)$$

Fig. 7 shows the calculated diffusion coefficients, D , for the unmodified parent coatings (control) and coatings modified using 1 or 10 wt.% BB as a function of temperature for each of the permeants. For temperatures $\leq 50^\circ\text{C}$, D for the modified coatings was similar to that of the parent coating, independent of permeant. At 70 – 75°C , D for 2-CEES, DMMP, DIMP, and MS through the parent

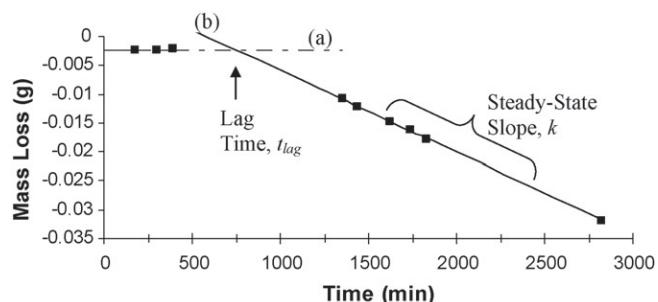


Fig. 6. Mass loss vs. time plot for the control coating using DIMP as the permeant at 60°C . The data are fit with two lines representing a constant-mass region (a) and a region of constant-mass loss (b). The intersection of the two lines gives the lag time, t_{lag} .

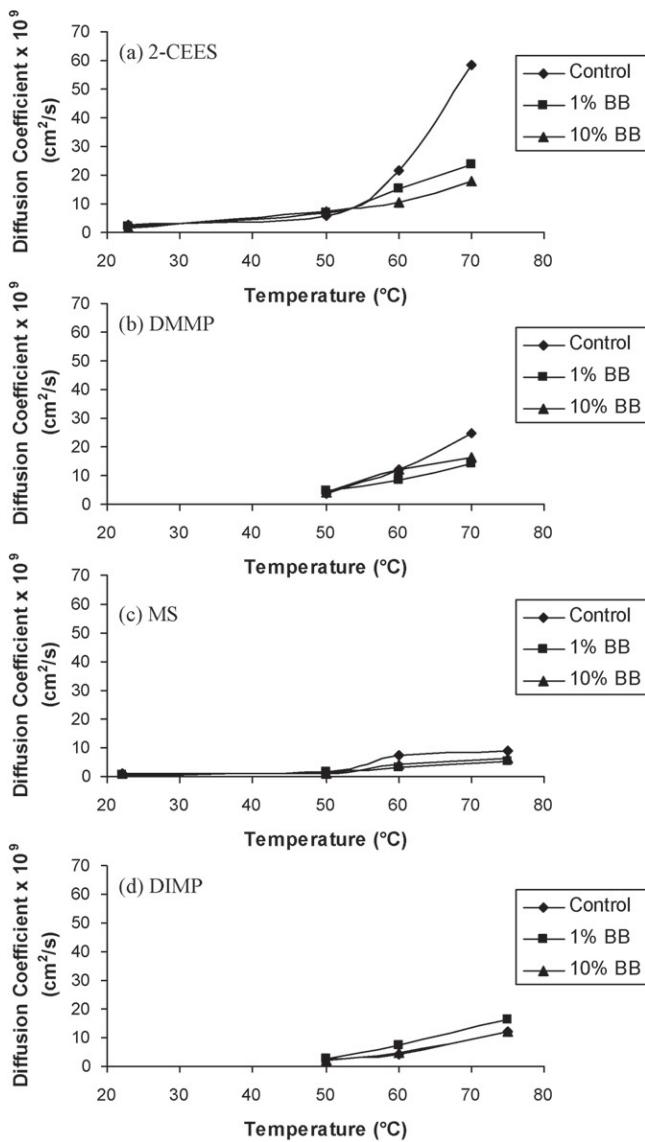


Fig. 7. Diffusion coefficient as a function of temperature for (a) 2-CEES, (b) DMMP, (c) MS, and (d) DIMP through coatings containing 1–10 wt.% BB.

coating were 5.8×10^{-8} , 2.4×10^{-8} , 1.2×10^{-8} , and $9 \times 10^{-9} \text{ cm}^2/\text{s}$, respectively. For the 10% BB modified coatings at 70–75 °C, D were 1.8×10^{-8} , 1.6×10^{-8} , 1.2×10^{-8} and $6.2 \times 10^{-9} \text{ cm}^2/\text{s}$ for 2-CEES, DMMP, DIMP, and MS, respectively. As compared to 2-CEES and DMMP, the decrease in the diffusion coefficient for the larger permeants, MS and DIMP, at 60–75 °C through the silane-modified coatings was less significant.

3.3.2. Physical characteristics

As determined using DSC, the addition of the silane modifier resulted in an increase of T_g from 14.78 °C for the parent PVB to 16.39 and 22.40 °C for coatings containing 1 and 10 wt.% BB, respectively. The increase in T_g is likely due to the formation of Si—O—Si linkages in the coating, as previously shown by Ji et al. [11] in epoxy coatings modified using γ -aminopropyltrimethoxysilane. Similar results were observed by Yin et al. [5], who investigated the T_g of interpenetrating networks of poly(methyl acrylate-co-2-hydroxyethyl acrylate) containing various concentrations of SiO_2 formed via sol-gel synthesis from TEOS. In their study, they observed an increase in T_g of approximately 6 °C upon addition of 10–20% TEOS to the polymer network. As previously reported

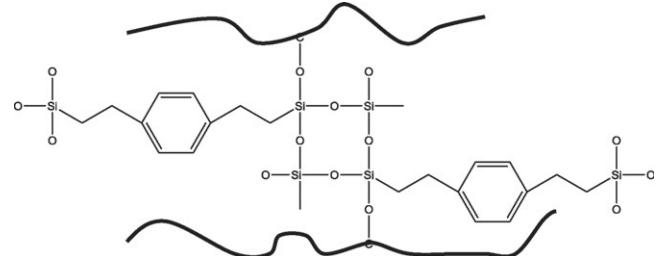


Fig. 8. Proposed representative structure of the organic-inorganic hybrid material formed through incorporation of BB into a PVB coating. The lines represent PVB polymer chains. The schematic is not drawn to scale.

by Chan et al. the observation of a single T_g indicates a single-phase morphology of the bis-silane modified coatings on a scale not smaller than 150 \AA^3 , indicating that the silane is well-dispersed within the parent coating.

The observed tensile strengths for the coatings were 1866, 2202, and 3391 psi for the parent, 1% BB, and 10% BB coatings, respectively. Percent elongation for the coatings was 40, 37, and 25% for the parent, 1% BB, and 10% BB coatings, respectively. Pencil hardness for the parent and 1% BB coatings were 6B. Coatings containing 10% BB exhibited a pencil hardness of 4B. Qualitative coating flexibility was determined using the mandrel bend test at 0 and -15 °C; no cracking of the coatings was observed at either temperature. Abrasion resistance was determined using a rotary abrader; loss of dry film thickness was 6.4, 6.1, and 4.8 μm (2.5, 2.4, and 1.9 mil) for the parent, 1% BB, and 10% BB coatings, respectively. These results indicate significant changes in the performance characteristics of the parent coating upon addition of the silane modifier.

4. Conclusions

The addition of 1–10 wt.% BB to a commercially available PVB coating resulted in the formation of a hybrid material containing silicate moieties covalently bonded to the polymer chains. Fig. 8 shows a representative structure of the modified coating prepared in this study. The proposed structure contains silsesquioxane units dispersed in and covalently bonded to the polymer structure. Addition of 1–10 wt.% BB increased the glass transition temperature, as the bis-silane becomes covalently bonded to the parent coating through the condensation of alcohol groups on the polymer and Si—OH groups on the hydrolyzed silane. The decrease in diffusion coefficient observed upon addition of the silane likely resulted from a reduction in the molecular motions of the parent PVB coating, an increase in coating tortuosity, and/or a reduction of the coating pore size. Additionally, the incorporation of the silane resulted in increase in coating hardness and abrasion resistance, likely due to the presence of inorganic regions comprising primarily Si—O—Si bonding. The connectivity with the PVB polymer backbone imparted by the bis-silane may be responsible for the increase in tensile strength of the coatings containing 1–10 wt.% BB. It is interesting that the coating flexibility was not degraded at low temperatures due to the inherent brittleness of silicate materials. We postulate that the use of a bridged organically modified silane allowed enough separation between the inorganic portions of the silicates to impart flexibility in the coating even at 10% BB incorporation levels.

Acknowledgements

The authors acknowledge the Air Force Research Laboratory for financial support, Ms. Uttara Mazumdar for her assistance with physical testing of the coatings, Ms. Sue Broxson for assistance with

the permeation study, and Ms. Brittney English for assistance with the infrared spectroscopy.

References

- [1] T.C. Gilmer, P.K. Hall, H. Ehrenfeld, K. Wilson, T. Bivens, D. Clay, C. Endresz, *J. Polym. Sci.: Part A: Polym. Chem.* 34 (1996) 1025.
- [2] P.B. Leezenberg, C.W. Frank, *J. Am. Chem. Soc.* 7 (1995) 1784.
- [3] C.-K. Chan, I.-M. Chu, *Polymer* 42 (2001) 6823.
- [4] L. Mascia, A. Kioul, *Polymer* 36 (1995) 3649.
- [5] W. Yin, T. Gu, H. Liu, B. Yin, *Polymer* 38 (1997) 5173.
- [6] M.B. Patil, S.A. Patil, R.S. Veerapur, T.M. Aminabhavi, *J. Appl. Polym. Sci.* 104 (2007) 273.
- [7] V.V. Annenkov, E.N. Daniilovtseva, E.A. Filina, A.I. Mikhaleva, T.A. Skotheim, B.A. Trofimov, *Polym. Int.* 53 (2004) 772.
- [8] L. Prezzi, L. Mascia, *Adv. Polym. Technol.* 24 (2005) 91.
- [9] A. Seth, W.J. van Ooij, P. Puomi, T. Metroke, A. Apblett, *Prog. Org. Coat.* 60 (2007) 170.
- [10] W.G. Ji, J.M. Hu, J.-Q. Zhang, C.N. Cao, *Corros. Sci.* 48 (2006) 3731.
- [11] W.G. Ji, J.M. Hu, L. Liu, J.Q. Zhang, C.N. Cao, *Prog. Org. Coat.* 57 (2006) 439.
- [12] Y. Chen, S. Zhou, G. Gu, L. Wu, *Polymer* 47 (2006) 1640.
- [13] F.X. Perrin, V. Nguyen, J.L. Vernet, *Polymer* 43 (2002) 6159.
- [14] S. Lu, H. Zhang, C. Zhao, X. Wang, *J. Appl. Polym. Sci.* 101 (2006) 1075.
- [15] M. Sangermano, G. Malucelli, E. Amerio, R. Bongiovanni, A. Priola, A. Di Gianni, B. Voit, G. Rizza, *Macromol. Mater. Eng.* 291 (2006) 517.
- [16] A.K. Dhaliwal, J.N. Hay, *Thermochim. Acta* 391 (2002) 245.
- [17] S.A. Torry, A. Campbell, A.V. Cunliffe, D.A. Tod, *Int. J. Adhes. Adhes.* 26 (2006) 40.
- [18] L. Matějka, O. Dukh, J. Brus, W. Simonsick, B. Meissner, *J. Non-Crystalline Solids* 270 (2000) 34.
- [19] A. Bertoluzza, C. Fagnano, M.A. Morelli, V. Gottardi, M. Guglielmi, *J. Non-Cryst. Solids* 48 (1982) 117.
- [20] X. Li, T.A. King, *J. Non-Cryst. Solids* 204 (1996) 235.
- [21] D.L. Ou, A.B. Seddon, *J. Non-Cryst. Solids* 210 (1997) 187.
- [22] J. Méndez-Vivar, A. Mendoza-Bandala, *J. Non-Cryst. Solids* 261 (2000) 127.
- [23] George Socrates, *Infrared and Raman Characteristic Group Frequencies*, 3rd ed., Wiley, Chichester, England, 2001.
- [24] J.Y. Ying, J.B. Benziger, *J. Non-Cryst. Solids* 147–148 (1992) 222.
- [25] S. Pauly, in: J. Brandrup, E.H. Immergut, E.A. Grulke, A. Abe, D.R. Bloch (Eds.), *Polymer Handbook*, 4th ed., John Wiley & Sons, 1999.